REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggesstions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any oenalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
21-07-2017	Final Report	15-Sep-2012 - 14-Jun-2016

4. TITLE AND SUBTITLE
Final Report: Determination of the influence of electric fields upon the densification of ionic ceramics

5a. CONTRACT NUMBER
W911NF-12-1-0491

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS
Klaus van Benthem

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of California - Davis
Sponsored Programs
1850 Research Park Drive, Suite 300
Davis, CA 95618 -6153

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
62265-MS.27

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
We have used in-situ transmission electron microscopy to reproduce appropriate experimental conditions typical for field-assisted sintering, with the goal to identify mechanisms that lead to field-assisted densification. Following studies by Raj and co-workers initial experiments focused on 3wt% Y-stabilized ZrO2. This approach required the development of techniques to evaluate densification during through TEM imaging, and assisting the development of new techniques to expose nanoparticles to non-contacting electrostatic fields at temperatures as high as 900

15. SUBJECT TERMS
field assisted sintering, grain growth, densification

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Klaus van Benthem
UU	UU	UU	UU		19b. TELEPHONE NUMBER 530-752-5117

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

Final Report: Determination of the influence of electric fields upon the densification of ionic ceramics

ABSTRACT

We have used in-situ transmission electron microscopy to reproduce appropriate experimental conditions typical for field-assisted sintering, with the goal to identify mechanisms that lead to field-assisted densification. Following studies by Raj and co-workers initial experiments focused on 3wt% Y-stabilized ZrO_2. This approach required the development of techniques to evaluate densification during through TEM imaging, and assisting the development of new techniques to expose nanoparticles to non-contacting electrostatic fields at temperatures as high as 900 centigrade. We have also performed detailed microstructure characterizations of flash sintered samples of the same material, which was until then mostly absent from the literature. We discovered that electrode effects as well as inhomogeneous field strength throughout the green body during flash sintering lead to non-homogeneous microstructures. We expect that therefore physical properties may be inhomogeneous depending local distance to the electrodes during flash sintering processing. Characterization of physical properties was, however, outside the scope of this project.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
07/18/2017	1	Cecile, Bonifacio. Evidence for Surface Cleaning during Electric Field Assisted Sintering, Scripta Materialia, (08 2013): 769. doi: 304,004.00
07/18/2017	19	K. van Benthem, J.F. Rufner, C.S. Bonifacio, T.B. Holland, R.H. Castro. Local Current-activated Growth of Nanometric Nickel Pillars During In situ STM-TEM Experiments, Microscopy and Microanalysis, ( ): 504. doi: 1,050,533.00
07/18/2017	16	A.P. Lange, A. Samanta, H. Majidi, S. Mahajan, J. Ging, T.Y. Olson, K. van Benthem, S. Elhadj. Dislocation mediated alignment during metal nanoparticle coalescence, Acta Materialia, ( ): 364. doi: 1,050,527.00
07/18/2017	15	Wei Qin, Hasti Majidi, Jondo Yun, Klaus van Benthem, L. Gauckler. Electrode Effects on Microstructure Formation During FLASH Sintering of Yttrium-Stabilized Zirconia, Journal of the American Ceramic Society, ( ): 2253. doi: 1,050,523.00
07/18/2017	14	Wei Qin, Jondo Yun, Andrew M. Thron, Klaus van Benthem. Temperature gradient and microstructure evolution in AC flash sintering of 3 mol% yttria-stabilized zirconia, Materials and Manufacturing Processes, ( ): 1. doi: 1,050,522.00
07/18/2017	12	Harsh, Maheshwari. Robust Mesoporous Silica Compacts: multi-scale characterization ofmicrostructural changes related to physical-mechanical properties, Journal of Materials Science, (09 2015): 4470. doi: 374,236.00
07/18/2017	8	Klaus, van Benthem. Characterization of advanced materials for petrochemical engineering, Journal of Science and Technology of Mining and Geology, (08 2014): 0. doi: 335,957.00
07/18/2017	7	Hasti, Majidi. Quantitative analysis for in situ sintering of 3% yttria-stablized zirconia in the transmission electron microscope, Utramicroscopy, (06 2014): 35. doi: 335,955.00
07/18/2017	2	Jorgen, Rufner. Local current-activated growth of individual nanostructures with high aspect ratios, Materials Research letters, (08 2013): 10. doi: 304,007.00
07/18/2017	3	Bonifacio, Cecile. Time dependent dielectric breakdown of surface oxides during electric field-assisted sintering, Acta Materialia, (05 2013): 140. doi: 304,010.00
08/30/2013	6	Troy B. Holland, Umberto Anselmi-Tamburini, Amiya K. Mukherjee. Electric fields and the future of scalability in spark plasma sintering, Scripta Materialia, (07 2013): 0. doi: 10.1016/j.scriptamat.2013.02.047 304,328.00
10/20/2015	11	Hasti Majidi, Troy B. Holland, Klaus van Benthem. Quantitative analysis for in situ sintering of 3% yttria-stablized zirconia in the transmission electron microscope, Ultramicroscopy, (12 2014): 35. doi: 10.1016/j.ultramic.2014.12.011 374,227.00
10/20/2015	10	Hasti Majidi, Klaus van Benthem. Consolidation of Partially Stabilized, Physical Review Letters, (05 2015): 195503. doi: 10.1103/PhysRevLett.114.195503 374,226.00

10/20/2015	13	Hasti Majidi, Klaus van Benthem. Effects of non-contact electric fields on consolidation behavior of agglomerated yttria-stablized zirconia, Microscopy and Microanalysis, (08 2015): 754. doi: 374,237.00
TOTAL:	**14**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1) Invited talk entitled "In-situ electron microscopy: characterizing materials under relevant conditions" presented at Army Strategy Workshop, Baltimore, MD (December 2013)
2) Tutorial talk entitled "Studies of Electric Field Assisted Sintering by in-situ TEM" presented during Microscopy & Microanalysis, Portland, OR(August 2014)
3) Seminar talk entitled "Characterization & Evolution of Defect Structures under Applied Stress Fields" presented at Korean Institute for Ceramics and Technology, KICET, (November 2015)
4) Seminar talk entitled "Characterization & Evolution of Defect Structures under Applied Stress Fields" presented at Witts University, Johannesburg, South Africa (May 2016)
5) Invited talk entitled "(In-situ) TEM Characterization of microstructure evolution to elucidate mechanisms for densification and grain growth" presented at Gordon Research Conference (July 2016)

Number of Presentations: 5.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received		Paper
07/18/2017	4	Klaus, van Benthem. In situ Transmission Electron Microscopy Characterization of Interfaces under Externally Applied Stress Fields, Mergind Atomic and Continuum Analysis of Nanometer Length-Scale Metal-Oxide systems for Energy And Catalysis Applications. 20-APR-13, Haifa, Israel. : ,
07/18/2017	17	Klaus, van Benthem. In-situ TEM Investigations of Grain Boundary Formation through Electric Field Assisted Sintering, PACRIM10. 03-JUN-13, San Diego, CA. : ,
07/18/2017	18	Klaus, van Benthem. Local Current-activated Growth of Nanometric Nickel Pillars During In situ STM-TEM Experiments, Microscopy & Microanalysis. 01-AUG-13, Indianapolis, IN. : ,
07/18/2017	20	Klaus, van Benthem. Atomistic characterization of electric field assisted sintering using in situ transmission electron microscopy, THERMEC. 07-DEC-13, Las Vegas, NV. : ,
07/18/2017	21	Cecile, Bonifacio. Atomistic characterization of electric field assisted sintering using in situ transmission electron microscopy, THERMEC. 06-DEC-13, Las Vegas, NV. : ,
07/18/2017	22	Hasti, Majidi. Understanding mechanisms of electric field assisted sintering using a variety of in situ TEM experiments, MRS Spring Meeting. 22-APR-14, San Francisco, CA. : ,
07/18/2017	23	Majidi, Hasti. In situ TEM investigations of densification mechanisms during electric field assisted sintering, FEMMS 2013. 18-SEP-13, Lorne, Australia. : ,
07/18/2017	24	Klaus, van Benthem. ELECTRIC FIELD EFFECTS ON GRAIN BOUNDARY FORMATION AND GRAIN GROWTH, ECI Conference of Field Assisted Sintering. 06-MAR-16, Tomar, Portugal. : ,
07/18/2017	25	Klaus, van Benthem. Grain Boundary formation and grain growth during electric field assisted sintering, Electronic Materials Division Meeting, ACerS. 24-JAN-16, Orlando, FL. : ,
07/18/2017	26	Klaus, van Benthem. Grain Boundary formation and grain growth during electric field assisted sintering, PACRIM-11. 15-SEP-14, Juju Island, South Korea. : ,

TOTAL: **10**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

PI van Benthem will receive the Richard M Fulrath Award 2017 by the American Ceramic Society based on the results that emerged from this project.

Graduate Students

NAME	PERCENT_SUPPORTED	DISCIPLINE
Wei Qin	100	Materials Science & Engineering
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Hasti Majidi	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Klaus van Benthem	0.08	
Troy Holland	0.08	
FTE Equivalent:	**0.16**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:......	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Wei Qin (degree expected in 2017)

Total Number: **1**

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

1 a. Colorado State University - Ft. Collins

1 b. 601 South Howes St., 408 Universit

Fort Collins CO 805212807

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): Experimental work was carried out at UC Davis while co-PI Holland accepted a faculty p

Sub Contract Award Date (f-1): 9/15/12 12:00AM

Sub Contract Est Completion Date(f-2): 3/14/14 12:00AM

---

1 a. Colorado State University - Ft. Collins

1 b. Sponsored Programs

2002 Campus Delivery

Fort Collins CO 805232002

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): Experimental work was carried out at UC Davis while co-PI Holland accepted a faculty p

Sub Contract Award Date (f-1): 9/15/12 12:00AM

Sub Contract Est Completion Date(f-2): 3/14/14 12:00AM

Inventions (DD882)

Scientific Progress

Initially during this project we used in-situ transmission electron microscopy to reproduce appropriate experimental conditions typical for field-assisted sintering. Following studies by Raj and co-workers initial experiments focused on 3wt% Y-stabilized ZrO2. This approach required the development of techniques to evaluate densification during through TEM imaging, and assisting the development of new techniques to expose nanoparticles to non-contacting electrostatic fields at temperatures as high as 900 centigrade.

A new technique to quantitatively obtain densification curves by TEM
Studying particle-agglomerate systems compared to two-particle systems elucidates different stages of sin- tering by monitoring both pores and particles. We report on in situ sintering of 3% yttria-stablized zirconia particle agglomerates in the transmission electron microscope (TEM). Real-time TEM observations indicate neck formation and growth, particle coalescence and pore closure. A MATLAB-based image processing tool was developed to calculate the projected area of the agglomerate with and without internal pores during in situ sintering. We demonstrate the first densification curves generated from sequentially acquired TEM images. The in situ sintering onset temperature was then determined to be at 960 °C. Densification curves illustrated that the agglomerate projected area which excludes the internal observed pores also shrinks during in situ sintering. To overcome the common projection problem for TEM analyses, agglomerate mass- thickness maps were obtained from low energy-loss analysis combined with STEM imaging. The decrease in the projected area was directly related to the increase in mass-thickness of the agglomerate, likely caused by hidden pores existing in the direction of the beam. Access to shrinkage curves through in situ TEM analysis provides a new avenue to investigate fundamental mechanisms of sintering through directly correlating microstructural changes during consolidation with mesoscale densification behavior. This work was published in Ultramicroscopy Vol 152 (2015), page 35-43
Experimental proof that electrostatic fields can cause moderate densification
Electric field–assisted sintering techniques demonstrate accelerated densification at lower temperatures than the conventional sintering methods. However, it is still debated whether the applied field and/or resulting currents are responsible for the densification enhancement. To distinguish the effects of an applied field from current flow, in situ scanning transmission electron microscopy experiments with soft agglomerates of partially stabilized yttria-doped zirconia particles are carried out. A new microelec- tromechanical system–based sample support is used to heat particle agglomerates while simultaneously exposing them to an externally applied noncontacting electric field. Under isothermal condition at 900 °C, an electric field strength of 500 V=cm shows a sudden threefold enhancement in the shrinkage of the agglomerates. The applied electrostatic potential lowers the activation energy for point defect formation within the space charge zone and therefore promotes consolidation. Obtaining similar magnitudes of shrinkage in the absence of any electric field requires a higher temperature and longer time. This work was published in Physical Reviews Letters Vol 114 (2015), page 195503
In a collaboration with researchers at LLNL we have used our in-situ TEM expertise to assess nanoparticle rotation during thermal sintering.

Rotation during nanoparticle coalescence
Dislocation mediated alignment processes during gold nanoparticle coalescence were studied at low and high temperatures using molecular dynamics simulations and transmission electron microscopy. Particles underwent rigid body rotations immediately following attachment in both low temperature (500 K) simulated coalescence events and low temperature (~315 K) transmission electron microscopy beam heating experiments. In many low temperature simulations, some degree of misorientation between particles remained after rigid body rotations, which was accommodated by grain boundary dislocation nodes. These dislocations were either sessile and remained at the interface for the duration of the simulation or dissociated and cross-slipped through the adjacent particles, leading to improved co- alignment. Minimal rigid body rotations were observed during or immediately following attachment in high temperature (1100 K) simulations, which is attributed to enhanced diffusion at the particles' interface. However, rotation was eventually induced by {111} slip on planes parallel to the neck groove. These deformation modes led to the formation of single and multi-fold twins whose structures depended on the initial orientation of the particles. The driving force for {111} slip is attributed to high surface stresses near the intersection of low energy {111} facets in the neck region. The details of this twinning process were examined in detail using simulated trajectories, and the results reveal possible mechanisms for the nucleation and propagation of Shockley partials on consecutive planes. Deformation twinning was also observed in-situ using transmission electron microscopy, which resulted in the co-alignment of a set of the particles' {111} planes across their grain boundary and an increase in their dihedral angle. This constitutes the first detailed experimental observation of deformation twinning during nanoparticle coalescence, validating simulation results presented here and elsewhere. This work was published in Acta materialia Vol 120 (2016), page 364-378
Following the success of FLASH sintering published in the literature despite the absence of any extensive microstructure characterization we have initiated detailed investigations of electrode effects during flash sintering, and microstructure evolution during flash sintering.

Electrode Effects during FLASH Sintering
Systematic microstructural statistics for 3 mol% yttria-stabilized zirconia synthesized by both conventional sintering and flash sintering with AC and DC current were obtained. Within the gage section, flash sintered microstructures were indistinguishable from those synthesized by conventional sintering pro-cedures. With both techniques, full densification was obtained. However, from both AC and DC flash sintered specimens, heterogeneous grain size distributions and residual porosity were observed in the proximity of the electrodes. After DC sintering, an almost 400 times increased average grain size was observed near cathode compared to the gage section, unlike areas close to the anode. Concepts of Joule heating alone were not sufficient to

explain the experimental observations. Instead, the activation energy for grain growth close to the cathode is lowered considerably during flash sintering, hence suggesting that electrode effects can cause significant heterogeneities in microstructure evolution during flash sintering. Microstructural characterization further indicated that microfracturing during green-pressing and variations in contact resistance between the electrodes and the ceramic may also contribute to grain size gradients and hence local variations of physical properties. This work was published in Journal of American Ceramic Society Vol 99 (2016), page 2253

Microstructure Evolution during FLASH Sintering

Systematic statistical analysis of the microstructural changes in 3¿mol% yttria-stabilized zirconia was performed after flash sintering by alternating current (AC). The micrographs in the gauge section of the specimen were identical to those from DC flash sintered samples while no evident electrode effect was present for AC flash sintered samples. However, finite element modeling revealed a temperature gradient from the surface to the volume of the sintered body. Microstructure gradients, across the width of gauge section, were revealed for the AC flash sintered sample. Classical grain growth models due to Joule heating were insufficient in justifying the microstructural evolution under the simulated temperature distribution. Bimodal grain diameter distributions in flash sintered samples were observed. Therefore, it is proposed that faster grain growth mechanisms activated on a fraction of the grains by electric field/current occurred during flash sintering, and is responsible for the instantaneous grain growth. This work was published in Materials and Manufacturing Processes Vol 32 (2016), page 549

SUMMARY:

Funding by the Army Research Office has allowed us to perform unprecedented in-situ TEM experiments to for the first time proof that electrostatic fields can contribute to ceramic particle densification in the absence of any current flow. This was previously hypothesized in the literature, but no conclusive proof was heretofore available. To enable such experiments we had to develop new image analysis techniques to determine quantitative densification curves from TEM experiments that by design only consider powder agglomerates with limited size and under vacuum conditions. However, the results demonstrated the mechanisms leading to field-assisted densification. Another major contribution thanks to this project was the microstructure characterization of FLASH-sintered ceramics, highlighting electrode and field effects leading to inhomogeneities in density and grain size throughout the sintered body.

The results of this 3-year study were published with high visibility in 14 article, lead to at least 21 invited talks at international conferences and seminars, and resulted in the PI receiving the Richard Fulrath Award of the American Ceramic Society.

Technology Transfer

We have purchased electro-thermal devices form Protochips, Inc. located in Raleigh, NC. While the devices were still under development and proved inadequate for the required experiments, we have collaborated with the company to refine the devices. Our contribution was in the characterization of W electrodes on MEMS devices. Postdoc Majidi performed electrical resistance measurements of the electrodes before and after their utilization at 900 centigrade to quantitatively evaluate the field strength applied during our in-situ densification experiments.